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DYNAMIC ION EXCHANGE CHROMATOGRAPHY FOR SENSITIVE DETERMINATION OF RARE EARTHS IN STEEL

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June 1990

Project: 30.69.02
Analytical Methodology

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15 pp

MINERAL SCIENCES LABORATORIES
DIVISION REPORT MSL 90-56 (IR)

MICROMEDIA

90-07117/

KEYWORDS: HPLC, Rare earths, Steels, Dynamic ion exchange, Sensitive detection

DYNAMIC ION EXCHANGE CHROMATOGRAPHY for SENSITIVE DETERMINATION of RARE EARTHS in STEELS

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ABSTRACT

A high-performance liqud chromatographic procedure has been developed for the direct determination of rare-earth elements in steel. Optimization of the effective capacity of the dynamic ion exchanger and the increased sensitivity of a post column reaction with Arsenazo 111 permitted detection down to 0.1 ng g-1. The analysis of rare earths in N B S steel standards without pre-separation are shown.

INTRODUCTION

Rare-earth metals are widely used in steel and iron alloys. Studies on the effect of rare earths in steel to modify sulphide particle formation and produce a more malleable product during processing operations are carried out at CANMET. The major analytical techniques that have been used to determine rare-earths in steels include spectrophotometry (1), X-ray fluorescence (XRF) (2), and inductively-coupled plasma-emission spectrometry (ICP-ES) (3).These techniques can suffer from interelement interferences or lack of sensitivities when they are used directly without specific sample treatment.

High performance dynamic ion exchange chromatography has been used for the determination of rare earths and yttrium in uranium processing solutions (4,5). In these techniques a hydrophobic ion, which is present in the eluent, is dynamically sorbed on to the surface of a hydrophobic support to provide a charged surface that can be used for ion-exchange separations. It was shown that this technique offers a wide choice of parameters which be used to achieve a required separation.

In our initial work (6) to determine rare earths in steel by HPLC a pre-separation was used to overcome the interference of iron on the detection of small amounts of rare earths. This paper describes the results of an investigation of chromatographic and post-column reaction conditions for the direct separation and determination of ppm concentrations of rare earths in steels and iron alloys.

EXPERIMENTAL SECTION

HPLC Apparatus

The HPLC system consisted of a Spectra Physics SP-8100 pump with autosampler (Spectra Physics, Santa Carla, CA), Kratos SF 770 variable wavelength detector (Kratos Analytical Intruments

Ramsey, ND), Spectra Physics SP-4270 computing integrator, and a Kratos DS 650 data aquistion system. The stainless steel reactor used to mix the Arsenazo III reagent and the eluate has been described eleswhere (4). The regent solution was delivered to the reactor by a syringe pump (ISCO M314, Lincoln, NE). A pulse dampener, 7.5 cm x 4.6 mm column of 10 um styrene-divinybenze, was inserted before the reactor. The HPLC column for these studies was a 5-um Supelcosil LC-18, 4.6 mm x 15 cm, (Supelco Canada, Oakville, ON).

Reagents and Materials

All solutions were prepared with water which was freshly distilled and passed through a Milli Q water system (Millipore, Bedford, MA, USA). Standard solutions (1000 ug/mL) of the rare earths were prepared from 5/9's pure oxides (Aldrich, Milwaukee, WI). These oxides were ignited to constant weight at 950°C and dissolved in dilute nitric acid. Stock solutions (2M) of a-hydroxisobutyric acid (HIBA) and (.1M) of sodium n-octanesulfonate (OS) were purified by passing them through a purified strong cation exchange resin. The a-hydroxyisobutyric acid was also purified by distillation, (~100°C) under vacuum. Eluents were prepared by weighing the calculated amounts of stock solution and diluting to approximately 900 mL with water, after which the pH was adjusted to the desired value by addition of 5M sodium hydroxide, and the

solution diluted to 1 L. All vessels used to prepare and store eluents were of polypropylene plastic. A stock solution (0.5 g/L) of 2,7-bis((o-arsenophenyl)azo)-1,8-dihydroxy-naphtalene-3,6-disulfonic acid (Arenazo III) was made 5M in acetic acid. The postcolumn reagent solution was prepared by dilution of 100 mL of the Arsrnazo III stock solution to 1 L and filtered though a 0.45-um filter. Acids used for sample dissolution were commercially available high-purity acids .

Sample Dissolution

A 0.5 g sample of steel was heated in a mixture of 5 mL of HNO3, 4 mL of HCLO4, and 1 drop of HF at 90°C. The solution was then evaporated to near dryness at low hotplate temperature to remove excess HCLO4. The salts were dissolved with 0.75 mL of HNO3 and 10 mL of H2O, and the solution transferred to a 50-mL volumetric flask and diluted to volume.

HPLC Determination

A 50-uL sample loop on the HPLC injection valve was flushed with 1.0 mL of 2% v/v HNO3, and then with 200 uL of sample. The sample loop was then valved in line with the eluent. For gradient elution of the steel sample the solvent program was run from 0.1 mol.L-1 HIBA to 0.35 mol.L-1 HIBA over 8.5 min, at a flow of 1.5

mL.min-1. The concentration of the modifier, sodium n-octane sulphonate, was 0.03 mol.L-1. The pH of the eluents was adjusted with NaOH to 4.6. The eluted metal ions were detected at 658 nm after a post-column reaction with Arsenazo 111 at a flow rate of 0.5 mL.mim-1. The concentration of Nd, Pr, Ce, and La in a sample were calculated from peak area calibration curves prepared from standard solutions. Results were calculated by a Spectra-Physics SP-4270 computing integrator.

RESULTS and DISCUSSIONS

An example of the chromatogram obtained for the direct determination of Nd, Pr, Ce, and La in a sample of NBS standard reference steel 361 by dynamic ion exchange on a C18 reversed phase is shown in Fig. 1. The chromatogram shows the separation of the early eluting ferric ion, and of copper (0.05%) and nickel (2%) from the rare earths. Maganese (0.7%) shows as a small peak near La. The amouts of rare earths in this injected sample varied from 1.6 ng for Pr to 20.2 ng for Ce.

In our initial studies (6), the high concentration of Fe and the concentration of acid present from sample dissolution (-0.4M) caused distorted peak shape.This was caused by the disruption of equilibrium between the n-octanesulphonate modifier and the reversed phase (7). The effect was eliminated by an increase in

the modifier concentration to 0.03 mol/L. However, the iron produced a wide and trailing peak that interfered with integration of the later eluting rare earths. This was overcome by using a concentration of 0.1M HIBA for the starting eluent in the gradient elution program, and iron eluted as a narrow band near the solvent front.

Careful control of reagent and eluent conditions was found to be necessary to maintain good peak shape and acceptable precision of the HPLC technique. It has been reported that bacteria in the eluents can be a recurring problem and degrade column performance (5). Further investigation showed that extranious metals in the eluents could cause large disruptions in the baseline which interfered with peak integration. These metals accummulate on the column during the intial stage of the gradient elution program and then eluted from the column as the concentration of the complexing agent, HIBA, increased. These disruptive peaks were collected during blank gratient runs and analyed by ICP-MS. Results showed that reagent grade HIBA contained up to 20 ppm of Zn, 10 ppm ofCu and Pb, and less than 1 ppm of Ba. However, when a stock solution of HIBA was purified by passing it through a acid washed strong cation exchange resin, up to 10 ppm of Ba and Mo, and lesser amounts of Zr were found. A procedure (8) was adapted to cleanup the strong cation-exchange resin of transition and also post-transition metals. With proper attention to eluent purity the baseline stability was good, and this permitted reproducible peak

areas.

A sensitive postcolumn-reaction system was necessary for the direct determination of small amounts of the rare earths in steel samples. The baseline noise that is observed with postcolumn-reaction systems that use visible absorbance detectors for the determination of metal ions arises from two sources: (a) change in the flow rates of the eluent and colour-reagent (Arsenazo III) resulting from pump pulsations; (b) poor mixing of the eluent and colour reagent. The major contribution to baseline fluctuations was from flow pulsations produced by the dual-piston pump for eluent delivery. The ISCO syringe pump used for Arsenazo III delivery also contributed to the noise. This was caused by the mechanical gear drive, and the lower the flow rate, the greater the noise. A 7.5 cm x 4.6 mm column of 10 um styrene-divinylbenzene, inserted between the mixing tee and the syringe pump, produced an effective pluse dampening system. A higher back pressure (~350 psi) was obtained for the Arsenazo 111 flow, and this resulted in pulsations in the eluent flow at the mixing-tee to be reduced. The peak-to-peak baseline noise was reduced by a factor of five. This allowed the flow rate of the Arsenazo III to be reduced (0.5 mL min-1) and further increase sensitivity by a decrease in dilution of the solutes.

Changes in the post-column reaction system allowed detection at 0.02 AFS, and permitted more reproducible integration for small

amounts of rare earths. The peak-to-peak baseline noise obtained with this post-column reaction system was ~3.10-5 AU. The detection limits was approximately 0.2 ng of a rare earth in a 50 uL injected sample (3 x peak-to-peak baseline noise).

The results obtained for NBS steel standards 361 and 363 are shown in Table 2. The HPLC data were obtained from the average of 6 samples determined in duplicate. The average relative standard deviation was 2.5%. The concentration of rare earths was calculated from peak area calibration curves prepared from standards that did not contain iron to simulate the samples, and illustrates non-biased recovery of the metals by this HPLC system.

CONCLUSIONS

An important feature of this HPLC method is the saving in terms of analysis time, relative to spectrophotometric and emission spectrometric techniques. Preliminary separations are not required for the HPLC method, and six samples plus a series of standards can be processed in duplicate in under 2.5 hrs. Because the above chromatographic and detection conditions gave well-defined peaks and low detection for rare earths (~0.2 ug. g-1), it should be possible to determine rare earths in a variety of samples by HPLC. This is being studied for the direct determination of rare earths in rocks, ores, and residue samples.

ACKNOWLEDGMENT

The authors wish to recognize the assistance of Conrad Gregoire, Geological Survey of Canada, for the inductively-coupled plasma-mass spectrometric analyses.

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Fig.1.Direct injection of steel sample. Experimental conditions: Supelco LC-18 column; gradient program from 0.1 mol.L-1 HIBA to 0.35 mol.L-1 HIBA over 8.5 min, at 1.5 mL.min-1. Eluent at pH 4.6; modifier,1-octanesulfonate at 0.03 mol.L-1; detection at 6[illegible] nm after post-column reaction with Arsenazo 111; sample, 50 ul; sample dilution, 0.5 g in 50 ml.

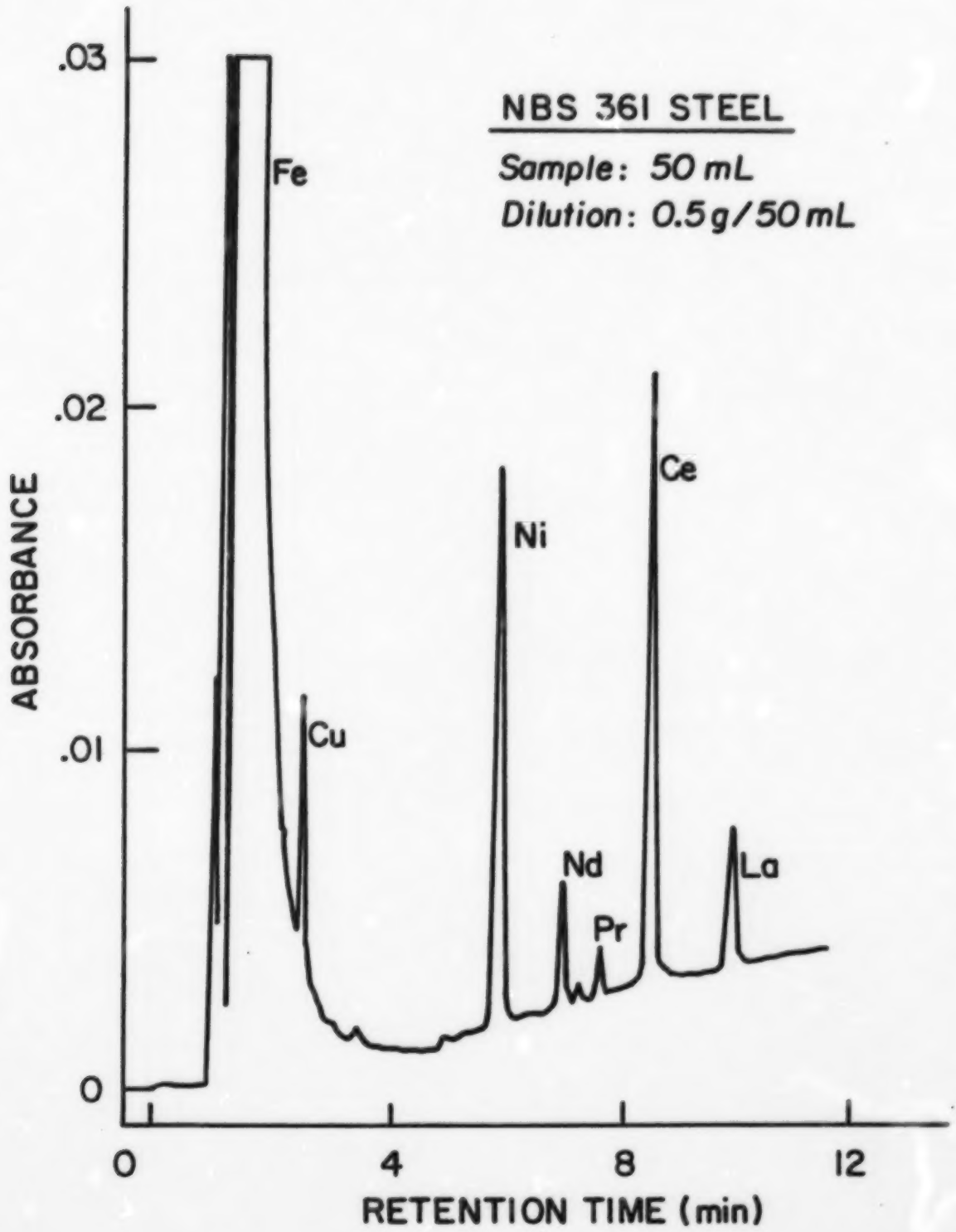
NBS 361 STEEL
Sample: 50 mL
Dilution: 0.5g/50mL
.03
.02
.01
0
ABSORBANCE
Fe
Cu
Ni
Nd
Pr
Ce
La
0
4
8
12
RETENTION TIME (min)

TABLE I.

ANALYSIS OF STEEL SAMPLES

STEEL SAMPLE	RARE EARTH	CERTIFIED ANALYSIS (WT %)	HPLC[A] ANALYSIS (WT %)	HPLC % RSD
NBS 361	Nd	0.0007_5	0.00081	1.7
	Pr	(0.0003)	0.00032	3.7
	Ce	0.0040	0.0041	0.8
	La	(0.001)	0.0010	2.0
NBS 363	Nd	0.0012	0.0011	2.7
	Pr	(0.0004)	0.00029	3.8
	Ce	0.0030	0.0028	4.3
	La	(0.002)	0.0011	1.8

[A]AVERAGE OF RESULTS OF SIX SAMPLES, EACH ANALYZED IN DUPLICATE.

VALUES IN PARENTHESES ARE NOT CERTIFIED.